SUPPORTING INFORMATION

Preparation of β -Keto esters and β -Diketones by C-Acylation/deacetylation of Acetoacetic Esters and Acetonyl Ketones with 1-Acylbenzotriazole

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Ethyl benzoylacetate (6a): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1, v/v); mp 265–270 °C [lit.¹¹] mp 265–270 °C]; yield 76%; keto tautomer: ¹H NMR (CDCl₃) δ 1.25 (t, J = 7.1 Hz, 3H), 4.00 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 7.44–7.52 (m, 2H), 7.56–7.63 (m, 1H), 7.92–7.98 (m, 2H); ¹³C NMR (CDCl₃) δ 14.0, 45.9, 61.4, 128.4 (2C), 128.7 (2C), 133.7, 135.9, 167.5, 192.5.

Ethyl (4-chlorobenzoyl)acetate (6b): colorless oil¹² after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1, v/v); yield 84%; keto tautomer: ¹H NMR (CDCl₃) δ 1.25 (t, J = 7.1 Hz, 3H), 3.97 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.89 (d, J = 8.7 Hz, 2H); ¹³C NMR (CDCl₃) δ 13.9, 45.8, 61.4, 129.0 (2C), 129.8 (2C), 134.2, 140.1, 167.1, 191.2.

Ethyl (4-methylbenzoyl)acetate (6c): colorless oil¹³ after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1, v/v); yield 85%; keto tautomer: ¹H NMR (CDCl₃) δ 1.26 (t, J = 7.1 Hz, 3H), 2.42 (s, 3H), 3.97 (s, 2H), 4.21 (q, J = 7.1 Hz, 2H), 7.28 (d, J = 7.8 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H); ¹³C NMR (CDCl₃) δ 13.9, 21.5, 45.8, 61.2, 128.5 (2C), 129.3 (2C), 133.4, 144.5, 167.5, 192.0.

Ethyl 3-(2-furyl)-3-oxopropanoate (6d): colorless oil¹⁴ after chromatography on silica gel using hexanes/ethyl acetate as eluant (10/1, v/v); yield 70%; keto tautomer: ¹H NMR (CDCl₃) δ 2.26 (t, J = 7.1 Hz, 3H), 4.86 (s, 2H), 5.21 (q, J = 7.1 Hz, 2H), 7.58 (dd, J = 3.6, 1.6 Hz, 1H), 8.28 (d, J = 3.6 Hz, 1H), 8.63 (d, J = 1.6 Hz, 1H); ¹³C NMR (CDCl₃) δ 13.9, 45.3, 61.4, 112.6, 118.2, 146.9, 151.8, 166.9, 180.9.

Ethyl (Z)-3-hydroxy-3-(4-pyridinyl)-2-propenoate (6e): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1, v/v); mp 55–57 °C [lit.¹⁵ mp 56–58 °C]; yield 71%; mixture of enol and keto forms (enol 61% in CDCl₃); enol tautomer: ¹H NMR (CDCl₃) δ 1.35 (t, J = 7.0 Hz, 3H), 4.29 (q, J = 7.0 Hz, 2H), 5.77 (s, 1H), 7.60 (AA'XX', J_{AX} = 6.4 Hz, 2H), 8.70 (AA'XX', J_{AX} = 6.4 Hz, 2H), 12.45 (s, 1H); ¹³C NMR (CDCl₃) δ 14.1, 60.7, 89.9, 119.6 (2C), 140.6, 150.8 (2C), 168.2, 172.5. keto tautomer: ¹H NMR (CDCl₃) δ 1.26 (t, J = 7.0 Hz, 3H), 4.00 (s, 2H), 4.22 (q, J = 7.0 Hz, 1H), 7.73 (AA'XX', J_{AX} = 6.1 Hz, 2H), 8.84 (AA'XX', J_{AX} = 6.1 Hz, 2H); ¹³C NMR (CDCl₃) δ 13.9, 45.9, 61.7, 121.1 (2C), 141.7, 151.0 (2C), 166.5, 192.0. Anal. Calcd for C₁₀H₁₁NO₃: C, 62.16; H, 5.75; N, 7.25. Found: C, 62.36; H, 5.76; N, 7.24.

Ethyl 3-oxooctanoate (6f): colorless oil¹⁶ after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1 $\approx$ 50/1, v/v); yield 58%; keto tautomer: ¹H NMR (CDCl₃) δ 0.89 (t, J = 6.8 Hz, 3H), 1.22–1.38 (m, 7H), 1.60 (p, J = 7.4 Hz, 2H), 2.53 (t, J = 7.4 Hz, 2H), 3.43 (s, 2H), 4.15–4.23 (m, 2H); ¹³C NMR (CDCl₃) δ 13.8, 14.0, 22.3, 23.1, 31.1, 42.9, 49.2, 61.2, 167.2, 202.9. Anal. Calcd for C₁₀H₁₈O₃: C, 64.47; H, 9.76. Found: C, 64.77; H, 10.03.

Ethyl 2-methyl-3-(4-methylphenyl)-3-oxopropanoate (8a): colorless oil¹⁸ after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1 $\approx$ 50/1, v/v); yield 76%; keto tautomer: ¹H NMR (CDCl₃) δ 1.17 (t, J = 7.1 Hz, 3H), 1.48 (d, J = 7.1 Hz, 3H), 2.42 (s, 3H), 4.15 (q, J = 7.1 Hz, 2H), 4.36 (q, J = 7.1 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.2 Hz, 2H); ¹³C NMR (CDCl₃) δ 13.7, 13.9, 21.6, 48.2, 61.2, 128.7 (2C), 129.4 (2C), 133.3, 144.3, 171.0, 195.5.

Ethyl 2-methyl-3-oxooctanoate (8b): colorless oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (100 : 50/1, v/v); yield 52%; keto tautomer: ^1H NMR (CDCl_3) δ 0.89 (t, $J = 7.0$ Hz, 3H), 1.22–1.36 (m, 10H), 1.59 (p, $J = 7.4$ Hz, 2H), 2.43–2.63 (m, 2H), 3.51 (q, $J = 7.2$ Hz, 1H), 4.19 (q, $J = 7.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 12.7, 13.8, 14.0, 22.4, 23.2, 31.2, 41.3, 52.8, 61.2, 170.6, 206.0; HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3$: m/z 200.1412. Found: 200.1412.

Ethyl 2-benzyl-3-(2-furyl)-3-oxopropanoate (8h): colorless oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (3/1, v/v); yield 69%; keto tautomer: ^1H NMR (CDCl_3) δ 1.14 (t, $J = 7.1$ Hz, 3H), 3.31 (d, $J = 7.7$ Hz, 2H), 4.08–4.16 (m, 2H), 4.41 (t, $J = 7.7$ Hz, 1H), 6.51–6.52 (m, 1H), 7.15–7.28 (m, 6H), 7.58 (d, $J = 1.5$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 34.2, 56.2, 61.4, 112.5, 118.6, 126.5, 128.4 (2C), 128.9 (2C), 138.1, 147.0, 151.8, 168.9, 183.0. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_4$: C, 70.57; H, 5.93. Found: C, 70.21; H, 6.00.

Ethyl 2-benzyl-3-oxo-3-(2-thienyl)propanoate (8i): colorless oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (3/1, v/v); yield 71%; keto tautomer: ^1H NMR (CDCl_3) δ 1.14 (t, $J = 7.1$ Hz, 3H), 3.27–3.40 (m, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 4.45 (t, $J = 7.5$ Hz, 1H), 7.08–7.11 (m, 1H), 7.15–7.28 (m, 5H), 7.65 (dd, $J = 5.1, 1.1$ Hz, 1H), 7.75 (dd, $J = 3.9, 1.1$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.9, 34.7, 57.4, 61.6, 126.6, 128.2, 128.5 (2C), 128.9 (2C), 133.0, 134.8, 138.2, 143.4, 168.9, 186.9. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_3\text{S}$: C, 66.63; H, 5.60. Found: C, 66.53; H, 5.64.

Ethyl 2-benzyl-3-oxo-3-phenylpropanoate (8j): colorless oil²¹ after chromatography on silica gel using hexanes/ethyl acetate as eluant (400/1 : 100/1, v/v); yield 65%; keto

tautomer: ^1H NMR (CDCl_3) δ 1.11 (t, $J = 7.1$ Hz, 3H), 3.33 (dd, $J = 7.5, 1.5$ Hz, 2H), 4.06–4.14 (m, 2H), 4.62 (t, $J = 7.5$ Hz, 1H), 7.17–7.29 (m, 5H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.5$ Hz, 1H). 7.96 (dd, $J = 7.5, 1.5$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.9, 34.7, 56.1, 61.4, 126.6, 128.4 (2C), 128.5 (2C), 128.6 (2C), 128.9 (2C), 133.5, 136.1, 138.4, 169.2, 194.4. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.58; H, 6.44. Found: C, 76.46; H, 6.63.

Ethyl 3-(2-furyl)-2-methyl-3-oxopropanoate (8c): colorless oil¹⁹ after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1 $\approx$ 3/1, v/v); yield 71%; keto tautomer: ^1H NMR (CDCl_3) δ 1.20 (t, $J = 7.1$ Hz, 3H), 1.48 (d, $J = 7.1$ Hz, 3H), 4.15 (q, $J = 7.1$ Hz, 1H), 4.17 (q, $J = 7.1$ Hz, 2H), 6.57 (dd, $J = 3.6, 1.7$ Hz, 1H), 7.28 (dd, $J = 3.6, 0.7$ Hz, 1H), 7.61 (dd, $J = 1.7, 0.7$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.1, 14.0, 48.6, 61.3, 112.5, 118.1, 146.7, 151.7, 170.4, 184.7. Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$: C, 61.21; H, 6.18. Found: C, 61.02; H, 6.19.

Ethyl 2-methyl-3-oxo-3-(2-thienyl)propanoate (8d): yellow oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1 $\approx$ 3/1, v/v); yield 60%; keto tautomer: ^1H NMR (CDCl_3) δ 1.21 (t, $J = 7.1$ Hz, 3H), 1.51 (d, $J = 7.1$ Hz, 3H), 4.13–4.26 (m, 3H), 7.14–7.17 (m, 1H), 7.69 (d, $J = 4.9$ Hz, 1H), 7.79 (d, $J = 3.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.7, 13.9, 49.4, 61.3, 128.2, 132.7, 134.5, 142.9, 170.2, 188.4. Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{S}$: C, 56.57; H, 5.71. Found: C, 56.37; H, 5.71.

Ethyl 2-methyl-3-oxo-3-(2-pyridyl)propanoate (8e): colorless oil after chromatography on silica gel using hexanes/ethyl acetate as eluant (6/1 $\approx$ 3/1, v/v); yield 60%; keto tautomer: ^1H NMR (CDCl_3) δ 1.14 (t, $J = 7.1$ Hz, 3H), 1.50 (d, $J = 7.1$ Hz, 3H), 4.13 (q, $J = 7.1$ Hz, 2H), 4.71 (q, $J = 7.1$ Hz, 1H), 7.45–7.50 (m, 1H), 7.85 (td, $J =$

7.7, 1.6 Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 8.66 (d, $J = 4.8$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 13.1, 13.9, 47.3, 60.9, 122.3, 127.2, 136.9, 148.8, 152.1, 171.6, 197.4. Anal. Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_3$: C, 63.76; H, 6.34; N, 6.76. Found: C, 63.58; H, 6.33; N, 6.62.

The recovered **1a** (0.1 g, 0.45 mmol, 9%), by-product **14** (0.13 g, 0.81 mmol, 16%) and **8f** were isolated as the first, second and third fractions after chromatography on silica gel using hexanes/chloroform as eluant (3/1, v/v).

Ethyl 2-methyl-3-oxo-3-phenylpropanoate (8f): colorless oil²⁰; yield 54%; keto tautomer: ^1H NMR (CDCl_3) δ 1.17 (t, $J = 7.1$ Hz, 3H), 1.50 (d, $J = 7.0$ Hz, 3H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.38 (q, $J = 7.0$ Hz, 1H), 7.45–7.50 (m, 2H), 7.56–7.61 (m, 1H), 7.98 (dd, $J = 7.8, 1.3$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.6, 13.8, 48.2, 61.2, 128.5 (2C), 128.6 (2C), 133.3, 135.8, 170.8, 195.8. Anal. Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.89; H, 6.86. Found: C, 70.11; H, 6.94.

Ethyl 2-methyl-3-oxo-4,4-diphenylbutanoate (8g): colorless oil after chromatography on silica gel using hexanes/chloroform (6/1 $\approx$ 3/1, v/v) as eluant; yield 51%; keto tautomer: ^1H NMR (CDCl_3) δ 1.20 (t, $J = 7.1$ Hz, 3H), 1.31 (d, $J = 7.1$ Hz, 3H), 3.70 (q, $J = 7.1$ Hz, 1H), 4.09 (q, $J = 7.1$ Hz, 2H), 5.44 (s, 1H), 7.17–7.37 (m, 10H); ^{13}C NMR (CDCl_3) δ 13.0, 13.9, 52.4, 61.4, 63.1, 127.1, 127.5, 128.4, 128.8, 128.9, 129.2, 137.2, 138.1, 170.1, 203.5. Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{O}_3$: C, 76.99; H, 6.82. Found: C, 76.61; H, 6.81.

Ethyl (Z)-2-benzyl-3-hydroxy-5-phenyl-2-penten-4-ynoate (8k): colorless prisms after chromatography on silica gel using hexanes/ethyl acetate (100/1 $\approx$ 6/1, v/v) as eluant; mp 95–97 °C; yield 54%; enol tautomer: ^1H NMR (CDCl_3) δ 1.24 (t, $J = 7.2$ Hz,

3H), 3.80 (s, 2H), 4.20 (q, $J = 7.2$ Hz, 2H), 7.16-7.25 (m, 2H), 7.29-7.43 (m, 6H), 7.50-7.58 (m, 2H), 12.40 (s, 1H); ^{13}C NMR (CDCl_3) δ 14.0, 33.6, 61.1, 83.2, 97.5, 108.4, 121.0, 126.0, 128.2 (2C), 128.4 (2C), 128.5 (2C), 129.8, 132.1 (2C), 140.5, 153.3, 172.6. Anal. Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3$: C, 78.39; H, 5.92. Found: C, 78.08; H, 5.91.

Ethyl 2-benzyl-3-(4-chlorophenyl)-3-oxopropanoate (8l): colorless prisms after chromatography on silica gel using hexanes/chloroform (100/1 $\approx$ 12/1, v/v) as eluent; mp 56-58 °C; yield 53%; keto tautomer: ^1H NMR (CDCl_3) δ 1.12 (t, $J = 7.1$ Hz, 3H), 3.32 (d, $J = 7.3$ Hz, 2H), 4.09 (q, $J = 7.1$ Hz, 2H), 4.56 (t, $J = 7.3$ Hz, 1H), 7.16-7.28 (m, 5H), 7.41 (d, $J = 8.4$ Hz, 2H), 7.89 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.9, 34.6, 56.1, 61.6, 126.7, 128.5 (2C), 128.9 (2C), 129.0 (2C), 130.0 (2C), 134.5, 138.2, 140.0, 169.0, 193.3. Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{ClO}_3$: C, 68.24; H, 5.41. Found: C, 68.08; H, 5.43.

Compounds **11** and **10a** were obtained in the reaction of **9** with **1a** as the first and second fractions after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1, v/v).

(Z)-3-Hydroxy-1,3-diphenyl-2-propen-1-one (11): colorless prisms; mp 67–68 °C [lit.²³ 77–78 °C] yield 18%; enol tautomer: ^1H NMR (CDCl_3) δ 6.86 (s, 1H), 7.46–7.59 (m, 6H), 7.97–8.02 (m, 4H), 16.87 (br s, 1H); ^{13}C NMR (CDCl_3) δ 93.1, 127.1 (4C), 128.7 (4C), 132.4 (2C), 135.5 (2C), 185.7 (2C).²⁴ Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2$: C, 80.32; H, 5.40. Found: C, 79.93; H, 5.42.

(Z)-4-Hydroxy-4-phenyl-3-buten-2-one (10a): colorless prisms; mp 52–53 °C [lit.^{25b} 58 °C]; yield 55%; enol tautomer: ^1H NMR (CDCl_3) δ 2.20 (s, 3H), 6.18 (s, 1H), 7.42–

7.55 (m, 3H), 7.86–7.89 (m, 2H), 16.15 (br s, 1H); ^{13}C NMR (CDCl_3) δ 25.8, 96.7, 127.0 (2C), 128.6 (2C), 132.3, 134.9, 183.3, 193.8.²¹ Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.04; H, 6.23. Found: C, 74.36; H, 6.19.

(Z)-3-Hydroxy-1,3-bis(4-methylphenyl)-2-propen-1-one (10b): yellow needles after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1, v/v); mp 118–120 °C [lit.²⁶ 117–118 °C]; yield 97%; enol tautomer: ^1H NMR (CDCl_3) δ 2.42 (s, 6H), 6.81 (s, 1H), 7.28 (d, J = 8.3 Hz, 4H), 7.88 (d, J = 8.3 Hz, 4H), 16.98 (br s, 1H); ^{13}C NMR (CDCl_3) δ 21.6 (2C), 92.5, 127.1 (4C), 129.3 (4C), 132.9 (2C), 143.0 (2C), 185.4 (2C). Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2$: C, 80.92; H, 6.39. Found: C, 80.61; H, 6.39.

(Z)-3-Hydroxy-1,3-di(2-thienyl)-2-propen-1-one (10c): yellow prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1, v/v); mp 94–96 °C [lit.²⁷ 98 °C]; yield 100%; enol tautomer: ^1H NMR (CDCl_3) δ 6.53 (s, 1H), 7.15 (dd, J = 4.9, 3.8 Hz, 2H), 7.61 (dd, J = 4.9, 1.2 Hz, 2H), 7.77 (dd, J = 3.8, 1.2 Hz, 2H), 16.18 (br s, 1H); ^{13}C NMR (CDCl_3) δ 92.6, 128.2 (2C), 129.9 (2C), 131.9 (2C), 140.6 (2C), 178.7 (2C); Anal. Calcd for $\text{C}_{11}\text{H}_8\text{O}_2\text{S}_2$: C, 55.91; H, 3.42. Found: C, 55.78; H, 3.32.

Compounds **10b** (23%), **10d** and **12** were obtained from the reaction of **9** with a mixture of **1c** and **1d** (1/1) as the first, second and third fractions after chromatography on silica gel using hexanes/ethyl acetate as eluant (200/1 $\rightarrow$ 100/1, v/v).

(Z)-1-(2-furyl)-3-hydroxy-3-(4-methylphenyl)-2-propen-1-one (10d): yellow prisms; mp 56–58 °C; yield 52%; enol tautomer: ^1H NMR (CDCl_3) δ 2.41 (s, 3H), 6.57 (dd, J = 3.5, 1.7 Hz, 1H), 6.73 (s, 1H), 7.22 (dd, J = 3.5, 0.7 Hz, 1H), 7.27 (d, J = 8.2 Hz, 2H), 7.59 (dd, J = 1.7, 0.7 Hz, 1H), 7.85 (d, J = 8.2 Hz, 2H), 16.27 (br s, 1H); ^{13}C NMR

(CDCl₃) δ 21.6, 92.2, 112.6, 115.5, 127.0 (2C), 129.3 (2C), 131.9, 143.1, 145.9, 151.0, 177.1, 182.8. Anal. Calcd for C₁₄H₁₂O₃: C, 73.68; H, 5.31. Found: C, 73.98; H, 5.67.

(Z)-1,3-di(2-furyl)-3-hydroxy-2-propen-1-one (12): yellow prisms; mp 63–65 °C [lit.²⁴ 66–68 °C]; yield 24%; enol tautomer: ¹H NMR (CDCl₃) δ 6.58 (dd, *J* = 3.7, 1.7 Hz, 2H), 6.65 (s, 1H), 7.20 (dd, *J* = 3.7, 0.5 Hz, 2H), 7.61 (dd, *J* = 1.7, 0.5 Hz, 2H), 15.60 (br s, 1H); ¹³C NMR (CDCl₃) δ 92.1, 112.6 (2C), 115.5 (2C), 146.1 (2C), 150.2 (2C), 174.6 (2C); HRMS (EI) Calcd for C₁₁H₈O₄: *m/z* 204.0423. Found: 204.0421.

(Z)-4-hydroxy-4-phenyl-1-(phenylsulfanyl)-3-buten-2-one (13a): yellow prisms after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1, v/v); mp 53–54 °C [lit.²⁹ 49–51 °C]; yield 62%; enol tautomer: ¹H NMR (CDCl₃) δ 3.73 (s, 2H), 6.37 (s, 1H), 7.21–7.32 (m, 3H), 7.38–7.51 (m, 5H), 7.80–7.82 (m, 2H), 15.71 (br s, 1H); ¹³C NMR (DMSO-*d*₆) δ 39.3, 96.2, 126.3, 126.8 (2C), 128.6 (2C), 128.9 (2C), 129.0 (2C), 132.9, 133.4, 135.0, 180.8, 193.5. Anal. Calcd for C₁₆H₁₄O₂S: C, 71.07; H, 5.23. Found: C, 70.80; H, 5.11.

Reaction of **10a** with **1d** gave **11** (17%), **13b** and **12** (15%) as the first, second and third fractions after chromatography on silica gel using hexanes/ethyl acetate as eluant (100/1, v/v).

(Z)-1-(2-furyl)-3-hydroxy-3-phenyl-2-propen-1-one (13b): yellow prisms; mp 66–68 °C [lit.³⁰ 42 °C]; yield 61%; enol tautomer: ¹H NMR (CDCl₃) δ 6.58 (dd, *J* = 3.5, 1.6 Hz, 1H), 6.77 (s, 1H), 7.24 (dd, *J* = 3.5, 0.7 Hz, 1H), 7.44–7.57 (m, 3H), 7.61 (dd, *J* = 1.6, 0.7 Hz, 1H), 7.94–7.98 (m, 2H), 16.20 (br s, 1H); ¹³C NMR (CDCl₃) δ 92.7, 112.6, 115.8,

126.9 (2C), 128.6 (2C), 132.3, 134.6, 146.1, 151.0, 177.6, 182.4. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.72. Found: C, 72.61; H, 4.56.

Reaction of **10a** with **1g** gave **11** (16%), **13c** and **10c** (15%) as the first, second and third fractions after chromatography on silica gel using hexanes/ethyl acetate as eluant (400/1 $\approx$ 50/1, v/v).

(Z)-3-hydroxy-3-phenyl-1-(2-thienyl)-2-propen-1-one (13c): yellow prisms; mp 77–79 °C [lit.^{31a} 78–79°C]; yield 61%; enol tautomer: 1H NMR ($CDCl_3$) δ 6.69 (s, 1H), 7.17 (dd, J = 4.9, 3.9 Hz, 1H), 7.45–7.57 (m, 3H), 7.64 (dd, J = 4.9, 1.0 Hz, 1H), 7.81 (dd, J = 3.9, 1.0 Hz, 1H), 7.94 (dd, J = 8.0, 1.3 Hz, 2H), 16.31 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 93.1, 126.8 (2C), 128.3, 128.7 (2C), 130.3, 132.3, 132.6, 134.4, 142.2, 180.8, 183.0. Anal. Calcd for $C_{13}H_{10}O_2S$: C, 67.79; H, 4.39. Found: C, 67.69; H, 4.20.

Ethyl (E)-2-methyl-3-[(1-phenylcyclopropyl)carbonyloxy]-2-butenate (15a): reaction time 2 h; yield 28%; 1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3H), 1.30 (q, J = 3.7 Hz, 2H), 1.68 (q, J = 1.5 Hz, 3H), 1.69 (q, J = 3.7 Hz, 2H), 2.21 (q, J = 1.5 Hz, 3H), 4.17 (q, J = 7.1 Hz, 2H), 7.25–7.41 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.6, 14.2, 17.0 (2C), 19.2, 29.2, 60.5, 117.4, 127.5, 128.3 (2C), 130.5 (2C), 138.8, 156.8, 167.6, 171.6. Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.82; H, 7.01. Found: C, 70.99; H, 7.19.

Ethyl (E)-2-methyl-3-[2-(2-phenylethyl)phenylcarbonyloxy]-2-butenate (15b): reaction time 3.0 h; yield 27%; 1H NMR ($CDCl_3$) δ 1.33 (t, J = 7.1 Hz, 3H), 1.85 (q, J = 1.5 Hz, 3H), 2.41 (q, J = 1.5 Hz, 3H), 2.88–2.94 (m, 2H, BB' part of AA' BB' system), 3.27–3.32 (m, 2H, AA' part of AA'BB' system), 4.25 (q, J = 7.1 Hz, 2H), 7.16–7.35 (m, 7H), 7.48 (td, J = 7.5, 1.4 Hz, 1H), 8.05 (dd, J = 8.0, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ

12.9, 14.2, 19.5, 36.8, 38.1, 60.6, 118.1, 125.9, 126.2, 127.9, 128.3 (2C), 128.5 (2C), 131.2, 131.6, 132.8, 141.7, 144.9, 156.7, 163.9, 167.7. Anal. Calcd for C₂₂H₂₄O₄: C, 74.98; H, 6.86. Found: C, 74.97; H, 7.00.

Ethyl (*E*)-2-benzyl-3-(phenylcarbonyloxy)-2-butenate (15c): reaction time 3.5 h; yield 31%; ¹H NMR (CDCl₃) δ 1.21 (t, *J* = 7.1 Hz, 3H), 2.46 (t, *J* = 0.9 Hz, 3H), 3.66 (br s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 7.12–7.26 (m, 5H), 7.44–7.50 (m, 2H), 7.59–7.65 (m, 1H), 8.04–8.08 (m, 2H); ¹³C NMR (CDCl₃) δ 14.0, 19.5, 33.1, 60.7, 121.8, 126.0, 128.2 (2C), 128.4 (2C), 128.6 (2C), 129.0, 130.1 (2C), 133.8, 139.3, 157.5, 163.8, 167.2. Anal. Calcd for C₂₀H₂₀O₄: C, 74.06; H, 6.21. Found: C, 74.21; H, 6.43.

Ethyl (*E*)-2-benzyl-3-(*p*-tolylcarbonyloxy)-2-butenate (15d): reaction time 3.5 h; yield 31%; ¹H NMR (CDCl₃) δ 1.20 (t, *J* = 7.2 Hz, 3H), 2.42 (s, 3H), 2.46 (t, *J* = 0.9 Hz, 3H), 3.66 (s, 2H), 4.16 (q, *J* = 7.2 Hz, 2H), 7.12–7.28 (m, 7H), 7.93–7.97 (m, 2H); ¹³C NMR (CDCl₃) δ 14.0, 19.5, 21.7, 33.0, 60.6, 121.7, 125.9, 126.2, 128.2 (2C), 128.4 (2C), 129.3 (2C), 130.1 (2C), 139.3, 144.6, 157.6, 163.8, 167.1. Anal. Calcd for C₂₁H₂₂O₄: C, 74.53; H, 6.57. Found: C, 74.60; H, 6.69.

Ethyl (*E*)-2-benzyl-3-[(1-phenylcyclopropyl)carbonyloxy]-2-butenate (15e): reaction time 3.5 h; yield 36%; ¹H NMR (CDCl₃) δ 1.16 (t, *J* = 7.0 Hz, 3H), 1.25–1.29 (m, 2H), 1.62–1.65 (m, 2H), 2.29 (t, *J* = 0.8 Hz, 3H), 3.48 (br s, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 6.96–7.01 (m, 2H), 7.10–7.22 (m, 3H), 7.25–7.36 (m, 5H); ¹³C NMR (CDCl₃) δ 14.0, 17.1 (2C), 19.3, 29.2, 32.8, 60.5, 121.1, 125.9, 127.5, 128.1 (2C), 128.3 (2C), 128.5 (2C), 130.5 (2C), 138.5, 139.1, 157.5, 167.0, 171.8. Anal. Calcd for C₂₃H₂₄O₄: C, 75.80; H, 6.65. Found: C, 75.50; H, 6.75.